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INVESTIGATION OF BONDING IN OXIDE-FIBER (WHISKER)  
REINFORCED METALS

J.M. Noone, et al

General Electric Company  
Philadelphia, Pennsylvania

October 1967

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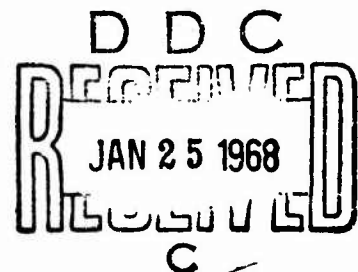
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# INVESTIGATION OF BONDING IN OXIDE-FIBER (WHISKER) REINFORCED METALS

SIXTH PROGRESS REPORT  
18 JULY 1967 - 18 OCTOBER 1967

M. J. Noone  
Willard H. Sutton  
18 OCTOBER 1967



Space Sciences Laboratory  
Missile and Space Division  
General Electric Company  
Philadelphia, Pennsylvania

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(WHISKER) REINFORCED METALS**

by

**M. J. Noone  
Willard H. Sutton**

18 October 1967

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### ABSTRACT

This work is part of a continuing study to determine the effects of various additives on the wetting and bonding of nickel and nickel alloys to single crystal sapphire ( $\alpha\text{-Al}_2\text{O}_3$ ). In previous work, using a sessile drop technique, small additions of Al, In, Cu, Cr, Ti, Zr, Ce, Y, and V were made to pure nickel and effects on both wetting and bonding were observed and several important parameters were identified.

In the present program, the effects of bonding interactions at the surface of flame-polished sapphire rods on the subsequent strength of the rods are being studied. Flame-polished rods with strength of  $5 \text{ to } 8 \times 10^5 \text{ lb in}^{-2}$  have been prepared and, with the exception of occasional large internal flaws, the strength was related to surface smoothness. The majority of the time and effort expended in this period has been devoted to the development of the flame-polishing technique since the use of high-strength rods is critical to the performance of the experiments planned for this program. Preliminary heat treatments of rods sputtered with Ni-alloy coatings indicate that slight interactions can degrade the sapphire surface and significantly reduce the strength of the rods. A study of interactions with specific alloying agents is in progress.

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## I. INTRODUCTION

This work is part of a continuing study of both the wetting and the bonding of nickel alloys to sapphire (single crystal  $\alpha$ - $\text{Al}_2\text{O}_3$ ). These factors are of critical importance in the development of high-strength  $\text{Al}_2\text{O}_3$ -fiber/Ni-base composite materials. The potential applications of such materials provide the stimulus for studies of the mechanisms of wetting and bonding, and of the influence of the nature of the bond, and any interface reaction, on the properties of the resultant composite.

A ceramic fiber with great potential as a reinforcing element, and which is readily available in high strength whisker form, is single crystal sapphire. However, the small size of whisker crystals precludes the performance of controlled experiments in which the details of wetting, bonding and interfacial reactions can be readily studied. Accordingly, previous work on this program has been performed on "massive" sapphire discs using sessile-drop techniques (1). Specially prepared nickel alloys containing controlled amounts (0.001 to a/o)\* of selected additives were melted on the sapphire discs and measurements of contact angle and apparent adherence were made (2). A few alloying elements (Cr, Ti, Zr) were studied in depth, and the microstructure of the interface was characterized by electron microscopy and electron probe microanalysis of the solidified specimens (3).

Results of the earlier work indicated that certain alloying elements segregated and became chemically active at the Ni/ $\text{Al}_2\text{O}_3$  interface. Enhanced bonding could result, but excessive interaction lead to the degradation of the sapphire surface and to the lowering of the apparent adherence. It was shown (2) that, to develop a strong bond between nickel and sapphire, the competing effects of strengthening by enhanced interfacial bonding, and weakening by degradation of the sapphire surface had to be optimized by a careful choice of additive and concentration. A model (2, 3) was proposed to equate these effects and was amply supported by the experimental data.

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\* a/o = atomic percent.

The crystallographic orientation of the sapphire disc has also been shown to influence the degree of wetting, and it has been suggested that an epitaxial relationship may exist between reaction product and the sapphire substrate (3).

A large amount of data has thus been assembled and some understanding of the parameters governing the wetting and bonding of nickel alloys to sapphire has been obtained. In recent work (4) a change in emphasis was made in an effort to relate the assembled data directly to the properties of a fiber composite system. For practical reasons, the experimental system again consisted of bulk sapphire specimens to avoid the difficulties associated with the study of effects at the surface of small crystals. Sapphire rods, 0.020" diameter and 2" or greater in length, were obtained, and their strength was measured in the "as-received" condition with both ground and flame-polished surfaces. The measured strength was, however, too low to allow experiments to be performed which could be directly compared with the behavior of high-strength whisker crystals. Therefore, a flame polishing rig was assembled in order to produce highly-polished smooth-surfaced rods under controlled conditions.

During the period covered by this report, the operation of the flame polishing rig was studied and a set of conditions was established such that high-strength rods could be readily obtained. Optimum conditions were probably not achieved, but rods with a high degree of surface perfection (smoothness) and with bend strength of  $5 \text{ to } 8 \times 10^5 \text{ lb in}^{-2}$  were produced. With the exception of occasional large internal flaws, the strength of the rods was directly related to surface perfection which could be readily assessed during the polishing operation. Preliminary studies of the effect of heat treatment on rods sputtered with Ni-alloy coatings indicate that interactions take place which degrade the sapphire surface and significantly reduce the strength of the rods. A systematic study of interactions between sapphire and nickel containing specific alloying agents is in progress and a study of a possible intermediate phase which will both protect the sapphire surface and promote wetting by the matrix is currently planned.



## II. EXPERIMENTAL

### 1. Development of the Flame-Polishing Technique

The small flame-polishing rig constructed in the previous period (4) has been operated under a wide range of conditions, so that the effects of each variable could be assessed and a suitable set of operating conditions chosen. The following sections describe the important factors governing the choice of conditions, the effect of changes in the major variables, and the operation and results of the process.

#### (a) Flame temperature

The gas supply to the flame consists of a stoichiometric mixture of hydrogen and oxygen generated by electrolysis of water. The two gases are never separated and are delivered to the burner in one line. The combustion temperature is about  $3300^{\circ}\text{C}$  but can be varied by the presence of water vapor or other vapors in the gas stream. Initially a hot flame, with the gases dried by a  $\text{CaCl}_2$  tower, was used; however, it was found that a greater degree of control could be obtained by using a cooler flame (about  $2500^{\circ}\text{C}$ ) produced by bubbling the gas stream through methyl alcohol. The flame was also rendered more visible by this procedure and had a clearly defined 'inner cone' which facilitated positioning the flame with respect to the rod. No difference in appearance of the rods or in their strength was detected between rods polished in the dry flame or in the slightly reducing 'alcohol' flame.

#### (b) Flame size

The size of the flame was determined by the size of the hypodermic needle jet and by the gas pressure: the addition of alcohol vapor increased the size of any given flame. The gas generator had a sensitive pressure gauge which was used to maintain a constant supply pressure of  $10 \text{ oz in}^{-2}$  (controlled by the voltage applied to the electrolytic cell). A range of jet sizes from No. 16 to 27 ( $0.0415''$  -  $0.0075''$  bore respectively) was used during the work. The larger jets provided a flame which was too large to be conveniently accommodated in the space available and provided a large excess of energy above that required to flame polish a slender rod. Flames from the

smaller jets were only capable of heating a small volume of the rod with a steep temperature gradient on either side of the hot spot. A jet size No. 23 (0.0125" bore) was found to provide a flame ~0.5" long x 0.05" diameter, inner cone 0.1" long, which was suitable for polishing the 0.020" diameter rods. The flame was large enough to envelope the rod and a length of about 0.020" of the surface appeared molten with a reasonably steep temperature gradient above and below the hot zone.

(c) Temperature of the rod surface

The temperature at the surface of the rods was determined by the distance of the burner jet from the rod and by the rate of movement of the rod through the flame. The distance from the rod was the most critical parameter in the production of well-polished rods and was controlled by the drive screw of the lathe toolpost on which the burner jet was mounted. The position of this screw could be read to  $\pm 0.002$ " and noticeable differences in surface appearance could be detected with changes of  $\pm 0.010$ " in the rod-to-jet distance.

The rod surface temperature changed appreciably with changes in the rate of movement of the rod through the flame. For this reason the rod-to-jet distance necessary to produce a good polish was adjusted to suit the speed of rotation of the rod: larger distances were needed for slower speeds.

Attempts to measure the temperature at the rod surface by optical pyrometry and to use this as a means of control were unsuccessful, since the area of material being heated was only about 0.020" square and the emissivity of the surface was continually changing as the initially ground surface was melted to form a smooth "glassy" one. It was soon realized that the simplest, practical means of assessing the optimum temperature and the quality of the polished surface was by visual observation of the rod through dark-glass 'welders' goggles.

(d) Lathe spindle rotation speed and flame traversing speed

The speed of rotation of the lathe spindle was varied from about 6 to 600 rpm using variac-controlled motors and a wide-range of pulleys and belts.

The lathe chuck was aligned such that the rod rotated within  $\pm 0.001''$  out of true about its long axis. The rate of traverse of the flame was directly linked via pulleys to the lathe spindle and initially was 1" of travel per 1000 revolutions. While it was realized that a high output rate would be desirable for the polishing process, it was thought in the early experiments that the best quality surfaces would be produced at low rotation rates. The initial work was therefore done on rods revolving at 1-20 rpm. Automatic traversing at these slow speeds produced only about  $0.02'' \text{ min}^{-1}$  of polished rod which was prohibitively low: manual fast traversing to approach about  $1/2'' \text{ min}^{-1}$  produced poorly polished surfaces. As a result of this, the spindle speed was progressively increased up to 600 rpm, which with the initial traversing gears gave  $0.6'' \text{ min}^{-1}$  of polished rod.

A predominant feature of this polishing process was a pronounced helical ripple coincident with the path traversed by the flame across the surface of the rod. This feature was recognized in earlier work on flame-polished sapphire (5) but was not found to prohibit the achievement of high strength. Nevertheless, it was considered desirable to reduce the effect as far as practicable and the traversing pulleys were changed to reduce the pitch of the helix to  $0.0005''$ . The rate of production of polished rod was thus reduced to  $0.3'' \text{ min}^{-1}$  and the majority of rods produced in this work have been polished at this rate; experience has however, indicated that, if necessary, higher polishing-rates (higher spindle speeds) would be practicable. Reduction of the pitch of the helix also reduced the depth of the furrows between the spiral traces and was therefore expected to increase the strength of the rods.

(e) Optimum polishing conditions

Good quality polished surfaces have been obtained from a wide range of polishing conditions so that the concept of an optimum set of conditions is not appropriate to this process (see also Ref. 6). It is evident that a balance must be established between the amount of heat supplied to the rod and the various sources of heat expenditure such that an optimum amount of molten  $\text{Al}_2\text{O}_3$  is maintained at the surface. The depth of the molten pool during

polishing is not known with certainty but is probably about 1-2 mils. The importance of heat conduction through the rod was demonstrated by the fact that it was found necessary to start polishing at a short distance ( $\sim 0.1''$ ) below the top of the rod so that heat was conducted away from the molten zone equally in both directions (up and down). Starting from the top, a flame that would normally produce a polished surface would melt the whole cross-section of the rod and form a progressively larger droplet as the flame travelled downward because of heat conduction away from the flame in one direction only.

(f) Summary of conditions used in the production of rods and the operating procedure

The following conditions were adopted for the production of the majority of the polished rods used in this work as a result of the experience described above.

- (i) Gas pressure 10 oz in<sup>-2</sup> with methyl alcohol vapor addition
- (ii) Jet size 0.0125" bore (hypodermic Jet No. 23)
- (iii) Jet-to-rod distance about 0.25": exact position determined by visual observation of the rod surface
- (iv) Rod rotation speed 600 rpm; flame traversing rate 0.0005" per revolution.

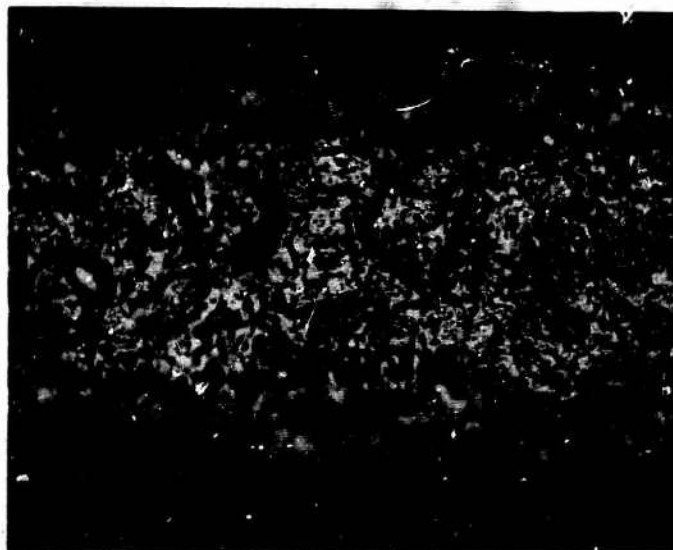
The molten  $\text{Al}_2\text{O}_3$  formed a collar round the rod about 0.020" wide by about 1-2 mils deep under these conditions. In operation, conditions (i), (ii) and (iv) were established, then the flame was brought to impinge on the rod  $\sim 0.1''$  from the top, the traverse engaged, and the jet-to-rod distance adjusted to produce the desired degree of polish. During polishing, the rod acted as a light-pipe for the intense source of illumination generated at the molten  $\text{Al}_2\text{O}_3$  and light scattering reflections were produced at any discontinuity within the rod or at its surface; these "flaws" were thus readily visible. Examination of rods during polishing was, therefore, the most sensitive means of assessing surface perfection and freedom from gross flaws. It was found that if too much  $\text{Al}_2\text{O}_3$  was melted during the process, coarse ripples

and "necking" of the rod occurred - in the extreme, the rod would resemble a string of beads. It was therefore found desirable to err on the side of under-polishing the rods on the first traverse of the flame and then to make a second (or more) traverse using a smaller jet-to-rod distance to remove any remaining traces of grinding marks in the surface. Although several rods appeared flaw-free after a single traverse, the majority required 2 or 3 passes. Examination of the rods following strength tests showed evidence of foreign particles in the surface and these often corresponded to the edge of fracture faces. An ultrasonic cleaning procedure was subsequently used prior to polishing: a detergent solution and then a water rinse was used and a marked improvement in the surface appearance (and in the strength) of the polished rods was observed. The "foreign" particles had obviously originated in dust and loose grinding debris present on the surface of the ground rods as received.

Both centerless-ground and commercially flame-polished rods were used in the rig and it was found that when using a ground rod it was easier to judge the correct polishing condition than when using a previously polished one. No advantage accrued from the use of commercially-polished rods and only the (cheaper) ground material was ordered for future work. Several rods were found to contain internal flaws (bubbles, inclusions etc.) which could not be removed by polishing; these internal flaws are sources of weakness in the rods and are to be avoided as far as possible in subsequent strength testing or in composite fabrication.

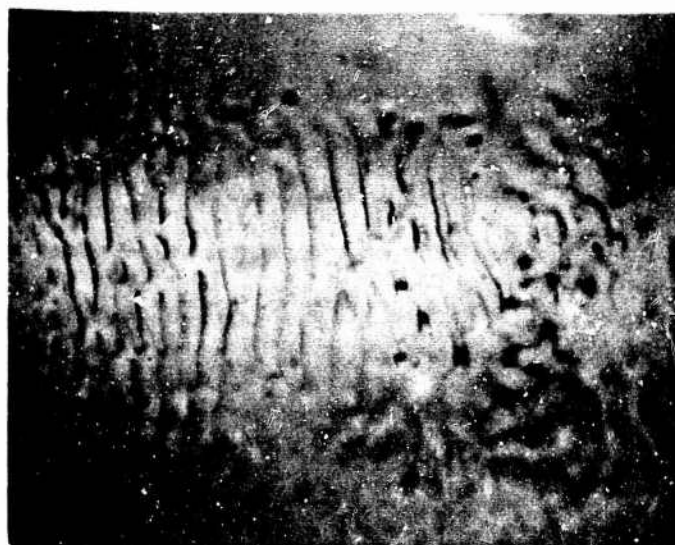
(g) Results of flame-polishing sapphire surfaces

Figure 1 shows the surface of a centerless-ground sapphire rod and illustrates the amount of surface roughness which has to be melted and recrystallized by the action of polishing. It can be seen that damage fragments have typical dimensions of ~1 mil in the direction of the surface and in depth. Figure 2 shows the surface of a ground rod after one pass of the flame under grossly "under-polished" conditions. The remnants of the grinding damage, although smoothed and rounded, are still evident and only slight increases in strength are to be expected at this stage. The right-hand



280X

Figure 1. The surface of a centerless-ground sapphire rod "as-received".



280X

Figure 2. The surface of a centerless-ground sapphire rod after one pass of a flame using "under-polishing" conditions.

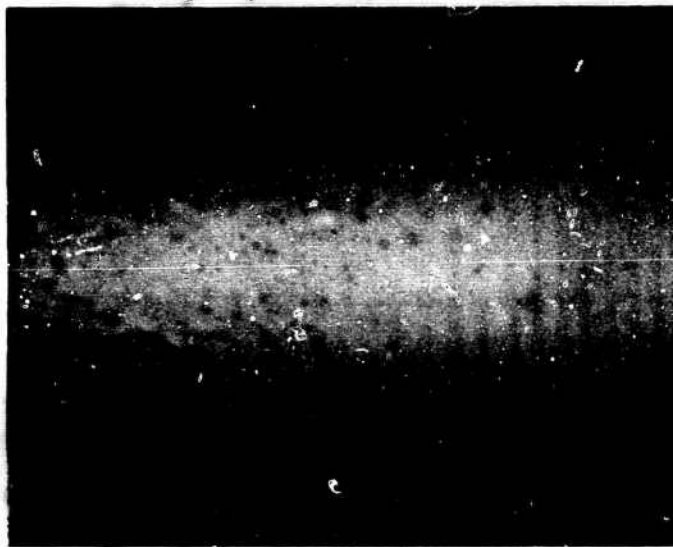
end of Figure 3 has been given a second pass of the flame and is well polished: the surface at the left-hand end contains many bubbles which seem to remain in the molten  $\text{Al}_2\text{O}_3$  collar to be swept down the rod by the liquid.

The surface of a commercially flame-polished rod 'as-received' is shown in Figure 4 (a and b). A large amount of grinding damage and remnants of 'dust' particles are still evident but an improvement in strength would be expected over that of a ground surface and was indeed found (4). No pronounced ripple is visible on the commercially-polished rods which indicates that only a small amount of  $\text{Al}_2\text{O}_3$  was liquid during polishing, and this appears to be insufficient in producing reproducibly high-strength rods.

The surface of a typical rod flame-polished in the present work under conditions described earlier is shown in Figure 5. The helical ripple is the only visible feature on such a surface. The varying width of the helical path is caused by slight changes in friction and slipping in the pulley-driven flame traversing system.

## 2. Strength of Flame-Polished Rods

The strength of the rods was measured using an Instron testing machine and 4-point (1" outer and 0.5" inner spans) and 3-point (0.5" span) bending rigs with rounded steel knife-edges. The Instron crosshead speed was  $0.002'' \text{ min}^{-1}$ . The initial tests were performed in 4-point bending and any fragments large enough were then tested in 3-point bending. Most rods suffered extensive fragmentation after fracture, some no doubt due to impact of the larger pieces with the bending rig. Some of this damage was reduced by draping the rod with small pieces of tissue paper which damped their motion and preserved larger fragments for further testing. No significant difference was detected between the results obtained from 4-point and those from 3-point test rigs: the spread in results was equally great and no distinction is drawn in the presented data. This indicates that a more uniform flaw-free surface is attained in the polishing operation compared to that of the commercial finishes when a significantly greater strength was measured in 3-point bending than in 4-point .

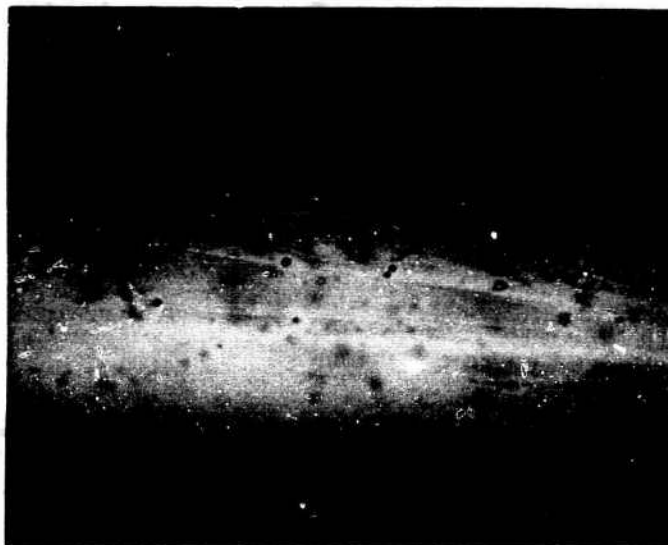


280X

**Figure 3.** The surface of a sapphire rod following flame-polishing. The right-hand side has received two passes of the flame and is well polished. The left-hand side is where the flame was removed and contains bubbles swept down the rod in the pool of molten  $\text{Al}_2\text{O}_3$ .



(a)



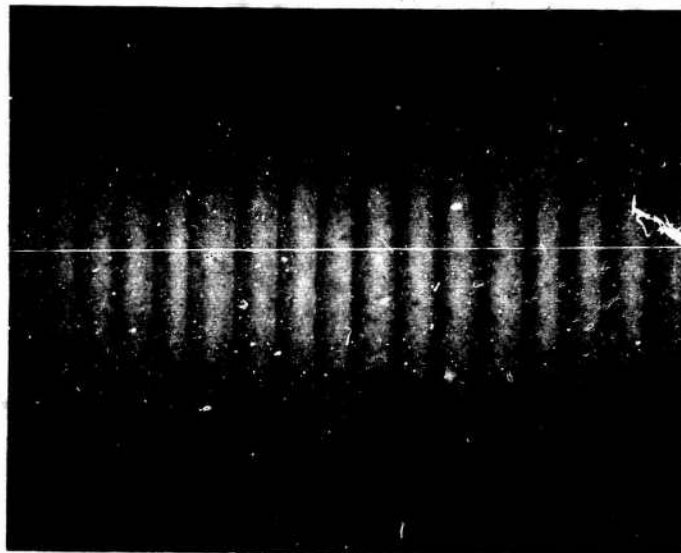
280X

(b)



280X

**Figure 4.** The surface of a commercially flame-polished rod. (a) Shows remnants of grinding damage and debris. (b) Shows "foreign" particles (dust?) and bubbles in the surface.



465X

Figure 5. The surface of a sapphire rod flame-polished under conditions described in the text.

Figure 6 shows the results obtained from the polished rods compared to those of the rods as received. The improvement in strength over the commercial rod is clearly shown: it was in fact very easy to improve on the commercial polish. A disturbing feature of some of the earlier work was the presence of coarse foreign particles or  $\text{Al}_2\text{O}_3$  grains in the surface of the rods. The origin of these particles was found to be dust and grinding damage on the as-received rods. When a cleaning procedure using an ultrasonic bath was employed, the lower strength results were eliminated and specimens with a minimum strength of  $500,000 \text{ lb in}^{-2}$  were obtained.

It is interesting to note that strengths of  $10^6 \text{ lb in}^{-2}$  attained in other work on flame-polished sapphire (5, 6) have not yet been achieved. There are two main reasons for this which suggest that the present rods may not be inferior to previous work. Firstly, no detailed selection of test gauge length was made, particularly for absence of internal defects which are known to be significant in fracture initiation at these high stress levels (5). Secondly, the test procedure used in this work does not offer protection to the specimens from contact with, or damage from, the loading system, although handling of the specimens and all contact with their surface was avoided as far as possible.

### 3. Effects of Heat Treatment Following Application of Sputtered Coatings on the Strength of Sapphire Rods

Sapphire rods polished as above and commercially polished (as-received), were coated with a sputtered layer of a Ni-Cr-Fe alloy about  $0.2\mu$  thick (7). This alloy (~60 Ni, 16 Cr, 24 Fe) is currently being used to coat sapphire whiskers to enhance wetting during fabrication of Al-matrix composites (7). During sputtering, the rods were held by their extreme ends and any contact with adjacent rods was avoided. As expected, no effect on strength as a result of the sputtering operation was found; a strength of  $8 \times 10^5 \text{ lb in}^{-2}$  was measured on a sputtered rod flame polished in this Laboratory.

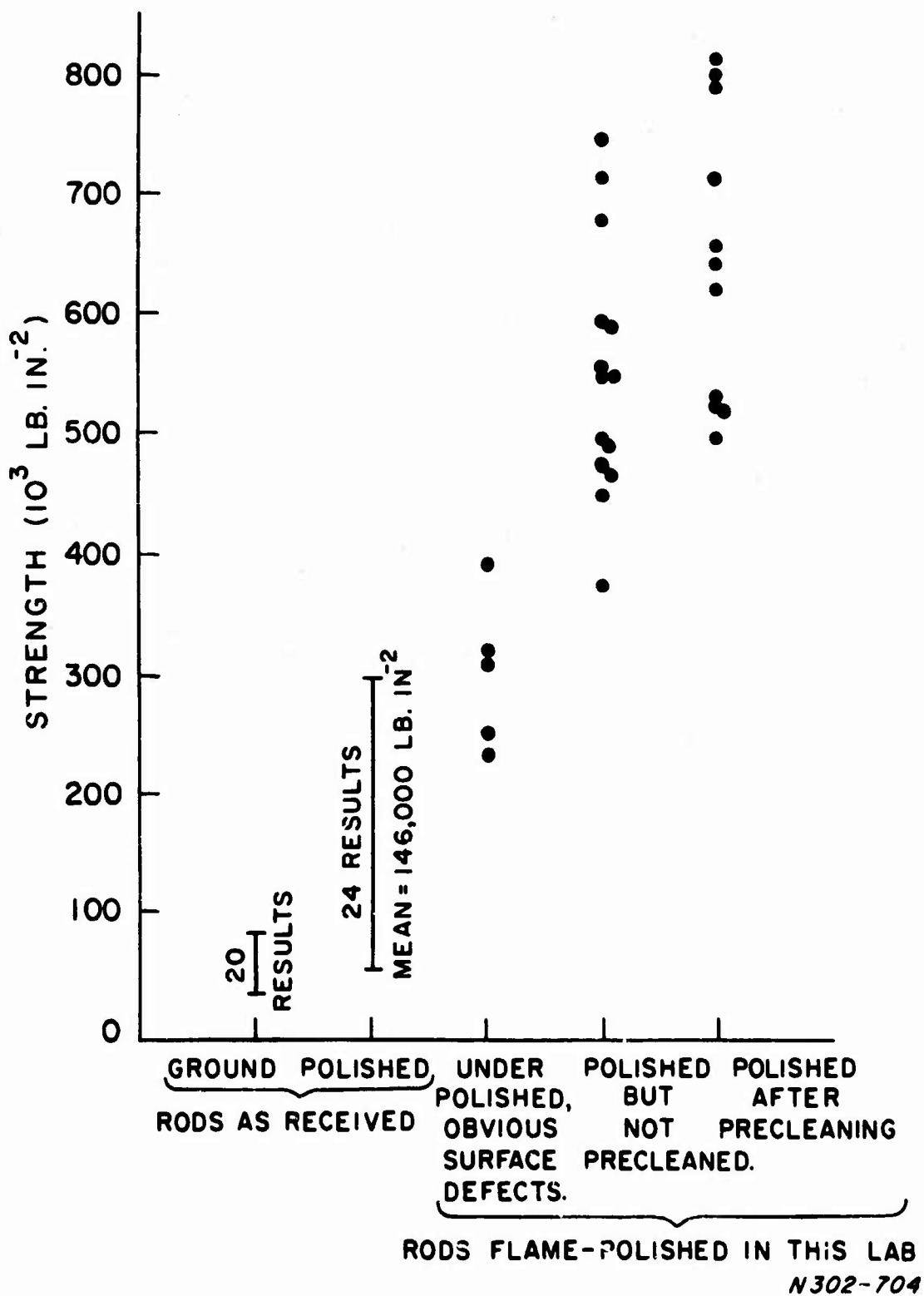


Figure 6. The strength of sapphire rods with various degrees of surface smoothness.

**(a) Heat treatment of sputtered 'as-received' rods**

The strength of sputtered commercially-polished rods following heat treatment is shown in Table 1, where additional experiments on unsputtered rods to determine whether any annealing was taking place, are also recorded. It can be seen that long-term heat treatment ( $1050^{\circ}\text{C}$  for 88 hrs in hydrogen) significantly increased the strength of the rods. A corresponding experiment on unsputtered rods showed that the strength increase could not be attributed to annealing but that some change in the nature and distribution of flaws in the surface was taking place as a result of the chemical interactions. It is suggested that the most pronounced flaws, possibly those due to foreign particles, are removed as a result of interactions, but that the new interface remains relatively rough (strength  $\sim 2 \times 10^5 \text{ lb in}^{-2}$ ). In a parallel experiment it was shown that the strength of rods with ground surfaces was increased by a similar annealing treatment. This can be attributed to removal of strain introduced by the grinding operation (6) but a similar annealing mechanism can obviously not operate after flame-polishing.

After heating to  $1500^{\circ}\text{C}$  for 20 minutes in hydrogen, the sputtered layer was separated into fine droplets. The strength of the rods was then reduced appreciably as a result of the attack by the liquid metal. The surface of rods heated in air was brown, glassy and fairly smooth; the strength was identical to that of the as-received rods.

**(b) Heat treatment of sputtered rods polished in this Laboratory**

The strength of sputtered, polished rods following various treatments is shown in Table 2. A significant result is the reduction in strength which followed after heating the Ni-Cr-Fe coating in hydrogen for 18 hrs at  $1000^{\circ}\text{C}$ . After heating, the coating had broken up to form a network of metal droplets as shown in Figure 7. Droplet formation did not occur on commercially polished specimens until heated to near the melting point of the alloy, and it is considered that the extreme smoothness of the flame polished surface contributed to the break up of the metal layer. The driving force for the formation of droplets is no doubt the desire to reduce the surface/volume ratio of the extremely thin film and the mechanism is presumably by surface

TABLE 1

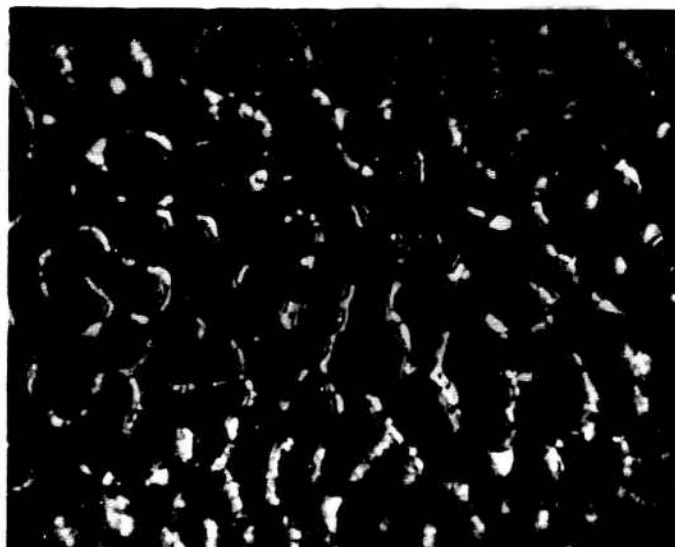
Strength of Commercially-Polished Rods After Various Heat Treatments.

History of Specimens	Mean Strength ( $10^3 \text{ lb in}^{-2}$ )	No. of Results
1. As received, before sputtering	146	24
2. After Ni-Cr-Fe sputtering	133	7
3. Ni-Cr-Fe coated & Heating to 1050°C for 88 hrs. in hydrogen	152	5
4. Ni-Cr-Fe coated & Heating to 1050°C for 88 hrs. in hydrogen	196	5
5. Uncoated & Heating to 1050°C for 88 hrs. in hydrogen	149	8
6. Ni-Cr-Fe coated & Heating to 1050°C for 16 hrs. in Air	148	5
7. Ni-Cr-Fe coated & Heating to 1500°C for 20 mins. in hydrogen	101	5
8. Ground surface as received	61	20
9. Ground surface & Heating to 1050°C for 88 hrs. in hydrogen	99	4

TABLE 2

Strength of Rods Polished in This Laboratory and After Receiving Various Heat Treatments and Coatings.

History of Specimens.	Mean Strength ( $\times 10^3$ lb in <sup>-2</sup> )	No. of Results
1. As polished	618	4
2. Ni-Cr-Fe coated & Heating to 1000°C for 18 hrs. in H <sub>2</sub>	245	4
3. As 2 above but metal removed in Aqua Regia before testing	375	2
4. Ni-Cr-Fe coated then coating removed in Aqua Regia	820	1
5. Ni-Cr-Fe coated & Heating to 1000°C for 66 hrs. in air	208	4
6. Ti coated & Heating to 1300°C in carbon-rich atmosphere to form TiC for 3 1/2 hrs.	120	8



1280X

Figure 7. A network of metal droplets formed on the surface of a flame-polished sapphire rod after coating with Ni-Cr-Fe and then heating to 1000°C for 18 hrs. in hydrogen.



diffusion. Mechanical locking of the layer onto the less well-polished surface prevents a similar break-up on the commercially polished surface.

Removal of the metal droplets revealed that considerable interaction had taken place beneath the drops and had considerably degraded the sapphire surface. Only slight attack was visible between drop sites indicating that the film probably broke-up early in the heating. Figure 8 shows the surface of a sapphire rod where droplets were removed in Aqua Regia. The extent of the interaction can be compared to that formed beneath a Ni + 1% Ti alloy droplet in earlier sessile drop experiments (3). The increase in strength after dissolution of the droplets implies that there was either a stress concentration at the junction of the droplets with the surface or that the acid treatment etched out stress raisers from the reaction-product surface layer. The former explanation is most likely and might account also for the low strength previously measured on droplet-covered rods (Condition 7, Table 1), although in that case the droplets were formed at a higher temperature. Acid treatment alone did not degrade the sapphire surface (Condition 4, Table 2), but it is thought unlikely that it would have improved it. However, only one data point is presently available on this aspect and it may not be significant.

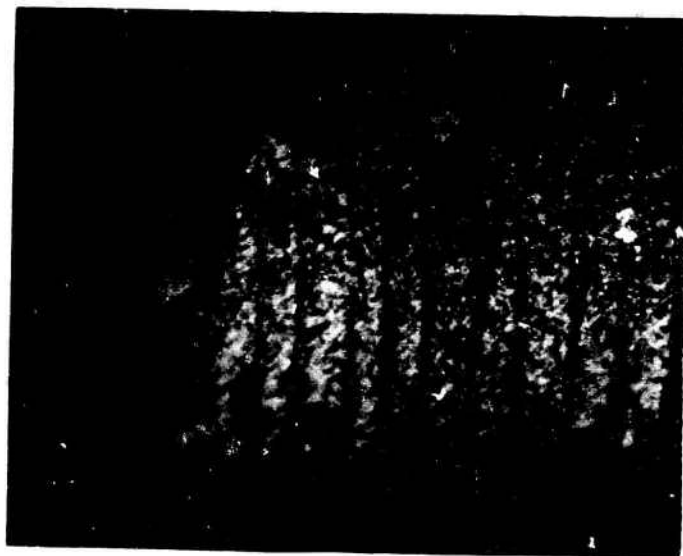
A sputtered Ti coating was applied to several rods in an experiment designed to study the possibility of formation of a TiC coating by heating in the presence of carbon. Recent work (8) has shown that TiC is reasonably compatible with sapphire and is wetted by Ni-Cr alloys. However, heating the rods in the presence of graphite produced a poorly adherent carbide layer and seriously degraded the sapphire surface. Since the carbide was previously found to be compatible with sapphire, it is concluded that the degradation was produced by reaction between Ti metal and  $Al_2O_3$  before the carbide was formed. The surface of the sapphire beneath the coating is shown in Figure 9, some TiC coating is adhering to the left-hand end of the rod. The degree of roughness resembles that of a ground or poorly-polished surface and the strength is proportionately low.



1280X

Figure 8. The surface of a sapphire rod after being subjected to the following procedures:

- (I) Flame polishing
- (II) Coating with Ni-Cr-Fe by sputtering.
- (III) Heating to 1000°C for 18 hrs. in hydrogen.
- (IV) Removal of the metal droplets (Fig. 7) by dissolution in aqua regia



1280X

Figure 9. The surface of a flame-polished sapphire rod following Ti sputtering and a carbonizing heat treatment to produce a TiC coating. The TiC coating has spalled off the right-hand side of the photograph.

### III. DISCUSSION AND FUTURE WORK

It has been shown that high-strength sapphire rods, which may be used in experiments as analogues of whisker crystals, can be produced fairly easily. It is also known (5) that, by careful selection of short lengths for freedom from internal defects, rods with highest strength and lowest scatter can be selected for specific experiments. The performance of controlled experiments to study the effects of various coatings and heat treatments is now possible and preliminary results obtained in this period have demonstrated the importance and relevance of surface reactions on the strength of the sapphire.

The particular alloy Ni-Cr-Fe used for this work may have been unnecessarily complicated by the presence of iron, and this certainly took part in the surface reactions: an iron containing spinel was detected following heating in air. A series of rods coated with pure metal and with nichrome without iron have been prepared for future studies and are awaiting heat treatment. It is hoped that a quantitative measure of the extent of interaction can be obtained from strength measurements and that the separate effects of particular alloying agents can be established. Two major areas of time and temperature require to be studied. Firstly, heating to high temperatures for short times to study the effects of degradation likely to be encountered during fabrication of composites by liquid infiltration techniques. Secondly, long time heatings at lower temperatures are necessary to assess the extent of reaction and degradation occurring during a 'service' life. The necessity of doing this type of experiment on high-strength rods was demonstrated in the results where it was seen that the strength of the commercially-polished rods appeared to change only slightly following certain heat treatments. This is because the resultant damage was of the same order, or less than, that originally present in the surface and the measured strengths were thus comparable. Similar degradation of a smooth high-strength surface was immediately detected as a severe lowering of strength.

As a result of the degradation found in these studies, some experiments are planned to explore the feasibility of coating the rods with a barrier layer which will both protect the sapphire surface from attack and promote wetting by the nickel alloys. Recent work has indicated that the carbides of Ti, V, and Zr are potential materials for this application (8) and it is planned to study these and other materials in future work.

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## REFERENCES

1. W.H. Sutton, "Investigation of Bonding in Oxide-Fiber (Whisker) Reinforced Metals," General Electric Co., M.S.D., U.S. Army Contract No. DA36-034-ORD-3786Z, Final Report No. AMRA CR 63-01/8, June 1964.
2. W.H. Sutton and E. Feingold, "Investigation of Bonding in Oxide-Fiber (Whisker) Reinforced Metals," General Electric Co., MSD, U.S. Army Contract No. DA19-066-AMC-184(x), Final Report No. AMCR 65-01/4, July 1965.
3. W.E. Sauer, W.H. Sutton and E. Feingold, "Investigation of Bonding in Oxide-Fiber (Whisker) Reinforced Metals," General Electric Co., MSD, U.S. Army Contract No. DA-19-066-AMC-330(x), Interim Report No. AMRA CR 66-01/4, May 1967.
4. M.J. Noone and W.H. Sutton, "Investigation of Bonding in Oxide-Fiber (Whisker) Reinforced Metals," General Electric Co., MSD, U.S. Army Contract No. DA-19-066-AMC-330(x), Fifth Quarterly Report No. AMMRC CR 66-01/5, July 1967.
- 5.(a) F.P. Mallinder and B.A. Proctor, "The Strengths of Flame-polished Sapphire Crystals," Phil. Mag., Vol. 13, No. 121, 197-208, 1966.
- 5.(b) B.A. Proctor, "The occurrence of specific stress-raisers in high-strength brittle solids," in "Physical Basis of Yield and Fracture," Ed. A.C. Strickland, Institute of Physics and the Physical Society (London), Conference Proceedings Series, No. 11, 1966.
6. F.P. Mallinder and B.A. Proctor, "Strengths of Sapphire Single Crystals," Rolls-Royce Research Report No. RR(OH)200, April 1965, Rolls-Royce Limited, Derby, England.
7. J. Chorne', C.A. Bruch, R. Jakas and W.H. Sutton, "Development of Composite Structural Materials for High Temperature Applications," General Electric Co., MSD, U.S. Naval Air Systems Command, Contract No. N00019-67-C-0243, 1st Quarterly Report, April 1967.
8. J. Chorne' and C.A. Bruch, "Development of Composite Structural Materials for High Temperature Applications," General Electric Co., MSD, Contract No. N00019-67-C-0243, 3rd Quarterly Report, September 1967.

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